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TWO UNEQUIVOCAL SYNTHESES OF 1′,2:3,6:3′,6′-TRIANHYDROSUCROSE

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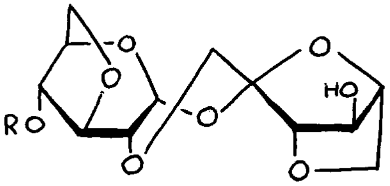
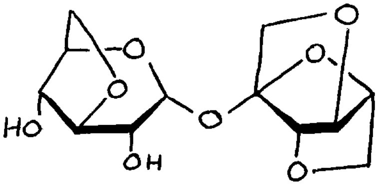
Abstract. *The title compound (1) has been synthesised via 1,2-anhydrosucrose and via 1,2-3,6-dianhydrosucrose and was found to be non-identical with the compound previously claimed to have this structure.*

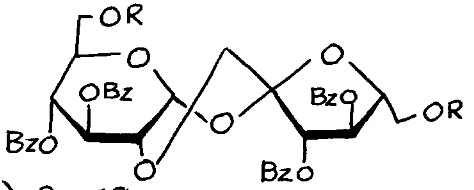
The supposed isolation of 1′,2:3,6:3′,6′-trianhydrosucrose (1) in 1959[1] by the action of base on a crude sucrose tritosylate (thought mainly to be the 1′,6,6′-isomer) has aroused considerable interest over the past decade. However, studies by Richards *et al.*[2] and then by Khan[3] established that 1′,6,6′-tri-O-tosylsucrose, and its esters, gave only the 1′,4′:3,6:3′,6′-trianhydride (3) rather than the bridged trianhydride (1). The suggestion[2] that (1) might have arisen from an isomeric tritosylate, such as the 2,6,6′-isomer, was invalidated by the work of Ball *et al.*[4] who demonstrated that the 2,6,6′-tritosylate, on alkaline alcoholysis, yielded a complex mixture. These authors concluded that (1) could not therefore originate by this route and they further suggested, with supporting evidence, that the trianhydride described by Lemieux and Barrette



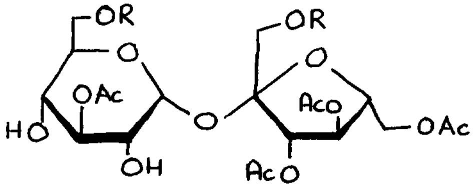
(1) R = H
(2) R = Ac



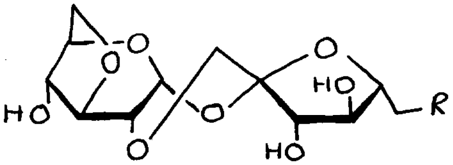
(3)



(4) R = CPh_3
(5) R = Ms



(6) R = H
(7) R = $O_2SC_6H_2Me_3$



(8) R = OH
(9) R = Br

was a lower melting isomorph of the 1′,4′:3,6:3′,6′-trianhydride (3). Since an unequivocal synthesis of the bridged trianhydride (1) was desirable, we have developed two different routes to this objective.

We have recently synthesised 1′,2-anhydrosucrose as its 6,6′-di-O-trityl derivative[5], benzoylation of which afforded the tetrabenzoate (4). Detritylation of (4) with hydrogen bromide in acetic acid followed by mesylation gave the 6,6′-dimesylate (5) in 84% overall yield. Intramolecular cyclisation of the 6,6′-dimesylate (5) was effected by sodium methoxide which gave the required 1′,2:3,6:3′,6′-trianhydride (1) [m.p. 189°, $[\alpha]_D$ +53.6° (MeOH)]in 80% yield, which was also characterised as its di-O-acetyl derivative (2) [m.p. 297-299° (decomp.), $[\alpha]_D$ +67.7° ($CHCl_3$)]. These data are clearly quite different from those recorded by Lemieux and Barrette[1] for their trianhydride [m.p. 163-164.5°, $[\alpha]_D$ +117° ($CHCl_3$); diacetate, m.p. 181.5-182.5°, $[\alpha]_D$ +128.5° ($CHCl_3$)] and show quite conclusively that their product was not the bridged trianhydride, but probably the lower melting isomorph of the 1′,4′:3,6:3′,6′-trianhydride (3) as previously suggested.[4]

An alternative approach to the synthesis of the trianhydride (1) utilised 3,3′,4′,6′-tetra-O-acetylsucrose (6)[6] as the starting material, which was readily available from 1′,2:4,6-di-O-isopropylidenesucrose. Selective mesitylenesulphonylation of the tetra-acetate (6) with 3 moles of mesitylenesulphonyl chloride afforded the required 1′,6-disulphonate (7) in 52% yield. Treatment of (7) with sodium methoxide afforded the syrupy 1′,2:3,6-dianhydride (8) in 68% yield. The structure of (8) was demonstrated by the ^{1}H-n.m.r. spectrum of its tetra-acetate [m.p. 115-116°, $[\alpha]_D$ +39° (chloroform)], which showed low field resonances due to H-3′ and H-4′ at δ 5.54 and 5.34 respectively, showing the presence of 3′- and 4′-O-acetyl groups which ruled out the possibility of an alternative 1′,4′:3,6-dianhydro structure. Selective mono-mesitylene sulphonylation of (8) was unsatisfactory since it afforded the 6′-sulphonate together with an unknown compound of identical chromatographic mobility, from which it could not be separated. However, placement of a leaving group at C-6′ was conveniently accomplished by bromination using carbon tetrabromide - triphenylphosphine[7] which afforded the 6′-bromide (9) in 42% yield. Alkaline methanolysis of (9) yielded the trianhydride (1), identical in all respects with the previous product.

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